

CLAIMS

What is claimed is:

1. An electrochemical cell array, said cell array comprising a plurality of nanoscale electrochemical cells wherein a cell comprising said array is a well having a cross-sectional area less than about $1 \mu\text{m}^2$, wherein a wall of said well comprises a first electrode and a second electrode said first electrode and said second electrode are separated by a non-conductor or semi-conductor, wherein the ratio of the surface area of said first electrode exposed to the interior of said well to the surface area of said second electrode exposed to the interior of said well is at least about 2:1.
- 10 2. The electrochemical cell array of claim 1, wherein said ratio is predetermined.
3. The electrochemical cell array of claim 1, wherein said ratio is at least about 5:1.
- 15 4. The electrochemical cell array of claim 1, wherein said well has a volume less than about $1 \times 10^{-14} \text{ L}$.
5. The electrochemical cell array of claim 1, wherein said array comprises at least 10 wells.
- 20 6. The electrochemical cell array of claim 1, wherein said array comprises at least 100 wells.
7. The electrochemical cell array of claim 1, wherein the center to center distance between two wells comprising said array is about 2.5 microns or less.
8. The electrochemical cell array of claim 1, wherein the center to center distance between two wells comprising said array is about 250 nm or less.
- 25 9. The electrochemical cell array of claim 1, wherein a plurality of the cells comprising said array are independently addressable.

10. The electrochemical cell array of claim 1, wherein said first electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.

11. The electrochemical cell array of claim 1, wherein said first electrode
5 comprises all the walls comprising said well.

12. The electrochemical cell array of claim 1, wherein said first electrode and said second electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.

13. The electrochemical cell array of claim 1, wherein said first electrode
10 comprises a material selected from the group consisting of copper, silver, chromium, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.

14. The electrochemical cell array of claim 1, wherein said second electrode comprises a material selected from the group consisting of copper, silver,
15 chromium, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.

15. The electrochemical cell array of claim 1, wherein said first electrode is a semiconductor.

16. The electrochemical cell array of claim 1, wherein said insulator or
20 semiconductor is an insulator.

17. The electrochemical cell array of claim 16, wherein said insulator is selected from the group consisting of silicon dioxide, and silicon nitride.

18. The electrochemical cell array of claim 1, wherein said second electrode has electrically coupled there to a redox active molecule.

25 19. The electrochemical cell array of claim 18, wherein said redox active molecule is attached to the second electrode via a linker.

20. The electrochemical cell array of claim 18, wherein said redox active molecule is attached to the second electrode via a linker bearing a sulfur.

21. The electrochemical cell array of claim 18, wherein said redox active molecule is attached to the second electrode via a linker bearing an alcohol.

5 22. The electrochemical cell array of claim 7, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a
10 flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

15 23. The electrochemical cell array of claim 7, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrinic sandwich complex, and a porphyrin array.

24. The electrochemical cell array of claim 8, wherein said organic molecule comprises a porphyrinic macrocycle substituted at a β - position or at a *meso*-position.

25. The electrochemical cell array of claim 1, wherein said second
20 electrode has electrically coupled thereto a binding partner.

26. The electrochemical cell array of claim 25, wherein said binding partner is selected from the group consisting of a nucleic acid, a protein, an antibody, a lectin, a carbohydrate, and a glycoprotein.

27. The electrochemical cell array of claim 1, wherein said first electrode
25 is a silver electrode, said second electrode is a gold electrode.

28. The electrochemical cell array of claim 27, wherein said second electrode has coupled thereto a redox-active molecule.

29. The electrochemical cell array of claim 27, wherein said second electrode has coupled thereto a binding partner.

30. The electrochemical cell array of claim 28 or claim 29, wherein said array comprises at least 100 cells.

5 31. The electrochemical cell array of claim 30, wherein said array is formed on a silicon substrate.

32. The electrochemical cell array of claim 30, wherein a plurality of the cells of said array are independently addressable.

10 33. A molecular memory, said memory comprising an electrochemical cell array, said cell array comprising a plurality of nanoscale electrochemical cells wherein a cell comprising said memory is a well having a cross-sectional area less than about typically less than 1 micron by 1 micron; wherein a wall of said well comprises a first electrode and a second electrode said first electrode and said second electrode separated by a non-conductor or semi-conductor, wherein the ratio of the surface area of said first electrode exposed to the interior of said well to the surface area of said second electrode exposed to the interior of said well is at least about 2:1; and wherein a redox-active molecule is electrically coupled to said second electrode.

20 34. The memory of claim 33, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

25 35. The memory of claim 34, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrin, an expanded porphyrin, a

contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrin sandwich complex, and a porphyrin array.

36. The memory of claim 35, wherein said organic molecule comprises a porphyrinic macrocycle substituted at a β - position or at a *meso*- position.

5 37. The memory of claim 33, wherein said ratio is predetermined.

38. The memory of claim 33, wherein said ratio is at least about 5:1.

39. The memory of claim 33, wherein said well has a volume less than about 10 femtoliters (10×10^{-15} L).

10 40. The memory of claim 33, wherein said array comprises at least 100 wells.

41. The memory of claim 33, wherein the center to center distance between two wells comprising said memory is about 250 nm or less.

42. The memory of claim 33, wherein a plurality of the cells comprising said memory are independently addressable.

15 43. The memory of claim 33, wherein said first electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.

44. The memory of claim 33, wherein said first electrode and said second electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.

20 45. The memory of claim 33, wherein said first and said second electrode are independently selected from the group consisting of copper, silver, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.

25 46. The memory of claim 33, wherein said first electrode is a semiconductor.

47. The memory of claim 33, wherein said insulator or semiconductor is an insulator.

48. The electrochemical cell array of claim 47, wherein said insulator is selected from the group consisting of silicon dioxide, silicon nitride.

5 49. The electrochemical cell array of claim 33, wherein said first electrode is a silver electrode, said second electrode is a gold electrode.

50. The electrochemical cell array of claim 49, wherein said array is formed on a silicon substrate.

10 51. The electrochemical cell array of claim 49, wherein a plurality of the cells of said memory are independently addressable.

52. A sensor comprising an electrochemical cell array, said cell array comprising a plurality of nanoscale electrochemical cells
wherein a cell comprising said sensor is a well having a cross-sectional area less than about 1 micron by 1 micron;

15 wherein a wall of said well comprises a first electrode and a second electrode said first electrode and said second electrode separated by a non-conductor or semi-conductor, wherein the ratio of the surface area of said first electrode exposed to the interior of said well to the surface area of said second electrode exposed to the interior of said well is at least about 2:1; and

20 wherein a binding partner is electrically coupled to said second electrode.

53. The sensor of claim 52, wherein said binding partner is selected from the group consisting of a nucleic acid, a protein, an antibody, a lectin, a carbohydrate, a glycoprotein.

25 54. The sensor of claim 52, wherein said sensor comprises at least two different binding partners, each species of binding partner in a different well.

55. The sensor of claim 52, wherein said sensor comprises at least ten different binding partners, each species of binding partner in a different well.

56. The sensor of claim 52, wherein said ratio is predetermined.
57. The sensor of claim 52, wherein said ratio is at least about 5:1.
58. The sensor of claim 52, wherein said well has a volume less than about 10 femtoliters (10×10^{-15} L).
59. The sensor of claim 52, wherein said sensor comprises at least 10 wells.
60. The sensor of claim 52, wherein said well is in fluid communication with a microchannel.
61. The sensor of claim 52, wherein the center to center distance between two wells comprising said array is about 2.5 microns or less.
62. The sensor of claim 52, wherein a plurality of the cells comprising said sensor are independently addressable.
63. The sensor of claim 52, wherein said first electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.
64. The sensor of claim 52, wherein said first electrode and said second electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.
65. The sensor of claim 52, wherein said first and said second electrode are independently selected from the group consisting of copper, silver, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.
66. The sensor of claim 52, wherein said first electrode is a semiconductor.
67. The sensor of claim 52, wherein said insulator or semiconductor is an insulator.

68. The sensor of claim 52, wherein said insulator is selected from the group consisting of silicon dioxide, silicon nitride.

69. The sensor of claim 52, wherein said first electrode is a silver electrode, said second electrode is a gold electrode.

5 70. The sensor of claim 52, wherein said wells are formed on a silicon substrate.

71. A method of making a nanoscale electrochemical cell, said method comprising:

10 depositing on a non-conducting substrate a first conductor;
depositing on said conductor a semiconductor or a nonconductor;
depositing on said semiconductor or a nonconductor a second conductor; and
15 forming a hole through said second conductor, said nonconductor or semiconductor, and said first conductor, whereby said hole forms a well having a cross-sectional area cross-sectional area less than about 1 micron by 1 micron, and said first conductor, said insulator or semiconductor, and said second conductor comprise a wall of said well.

20 72. The method of claim 71, wherein said non-conducting substrate is a non-conducting substrate selected from the group consisting of silicon dioxide, and silicon nitride.

73. The method of claim 71, wherein the first conductor is deposited by a method selected from the group consisting of electron beam evaporation, thermal evaporation, electrochemical reduction, and electroless deposition.

74. The method of claim 71, wherein the second conductor deposited by 25 a method selected from the group consisting of electron beam evaporation, thermal evaporation, electrochemical reduction, and electroless deposition.



75. The method of claim 71, wherein said depositing a first conductor comprises depositing a layer of conducting material and selectively removing regions of said conducting material to form a patterned conducting material.

76. The method of claim 71, wherein said depositing a second conductor
5 comprises depositing a layer of conducting material and selectively removing regions of said conducting material to form a patterned conducting material.

77. The method of any one of claims 75 or 76, wherein the selective removing comprising placing a patterned resist on said conductor and then etching said conductor.

10 78. The method of claim 71, wherein said first conductor comprises a silver layer.

79. The method of claim 71, wherein said second conductor comprises a chromium gold layer.

15 80. The method of claim 71, wherein said nonconductor or semiconductor comprises a dielectric.

81. The method of claim 71, wherein said hole is formed by a method selected from the group consisting of laser drilling, reactive ion etching (RIE), chemically assisted ion beam milling (CAIBM), and wet etching.

82. The method of claim 71, further comprising coupling a redox active
20 molecule to said second conductor.

83. The method of claim 71, further comprising coupling a binding partner to said second conductor.

84. The method of claim 71, wherein said hole is one of a plurality of holes.

85. The method of claim 71, wherein the ratio of the surface area of said first conductor exposed to the interior of said well to the surface area of said second conductor exposed to the interior of said well is at least about 2:1.
86. The method of claim 85, wherein said ratio is predetermined.
- 5 87. The method of claim 71, wherein said well has a volume less than about 10 femtoliters (10×10^{-15} L).
88. The method of claim 84, wherein said plurality of wells comprises at least 10 wells.
- 10 89. The method of claim 84, wherein the center to center distance between two wells comprising said array is about 2.5 microns or less.
90. The method of claim 71, wherein said first conductor comprises all the walls comprising said well except the bottom wall and, if present, a top wall.
- 15 91. The method of claim 71, wherein said first conductor and said second conductor comprise all the walls comprising said well except the bottom wall and, if present, a top wall.
92. The method of claim 71, wherein said first electrode comprises all the walls comprising said well.
- 20 93. The method of claim 71, wherein said first and said second conductor are independently selected from the group consisting of copper, silver, chromium, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.
94. The method of claim 71, wherein said first conductor is a semiconductor.
- 25 95. The method of claim 71, wherein said insulator or semiconductor is an insulator.

96. The method of claim 95, wherein said insulator is selected from the group consisting of silicon dioxide, silicon nitride.

97. A nanoscale electrochemical cell, said cell comprising a well having a cross-sectional area less than about typically less than 1 micron by 1 micron, wherein a
5 wall of said well comprises a first electrode and a second electrode said first electrode and said second electrode separated by a non-conductor or semi-conductor, wherein the ratio of the surface area of said first electrode exposed to the interior of said well to the surface area of said second electrode exposed to the interior of said well is at least about 2:1.

98. The electrochemical cell of claim 97, wherein said ratio is
10 predetermined.

99. The electrochemical cell of claim 97, wherein said ratio is at least about 5:1.

100. The electrochemical cell of claim 97, wherein said well has a volume less than about 10 femtoliters (10×10^{-15} L).

101. The electrochemical cell of claim 97, wherein said first electrode comprises all the walls comprising said well except the bottom wall and, if present, a top wall.

102. The electrochemical cell of claim 97, wherein said first electrode and said second electrode comprises all the walls comprising said well except the bottom wall
20 and, if present, a top wall.

103. The electrochemical cell of claim 97, wherein said first and said second electrode comprise a conductor independently selected from the group consisting of copper, silver, chromium, gold, platinum, a conducting polymer, aluminum, silicon, germanium, gallium arsenide, ruthenium, titanium and tantalum.

104. The electrochemical cell of claim 97, wherein said first electrode is a
25 semiconductor.

105. The electrochemical cell of claim 97, wherein said insulator or semiconductor is an insulator.

106. The electrochemical cell of claim 105, wherein said insulator is selected from the group consisting of silicon dioxide, silicon nitride.

5 107. The electrochemical cell of claim 97, wherein said second electrode has electrically coupled thereto a redox active molecule.

108. The electrochemical cell of claim 107, wherein said redox active molecule is attached to the second electrode via a linker.

10 109. The electrochemical cell of claim 107, wherein said redox active molecule is attached to the second electrode via a linker bearing a sulfur.

110. The electrochemical cell of claim 107, wherein said redox active molecule is attached to the second electrode via a linker bearing an alcohol.

15 111. The electrochemical cell of claim 107, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrinic macrocycle, a metallocene, a linear polyene, a cyclic polyene, a heteroatom-substituted linear polyene, a heteroatom-substituted cyclic polyene, a tetrathiafulvalene, a tetraselenafulvalene, a metal coordination complex, a buckyball, a triarylamine, a 1,4-phenylenediamine, a xanthene, a flavin, a phenazine, a phenothiazine, an acridine, a quinoline, a 2,2'-bipyridyl, a 4,4'-bipyridyl, a tetrathiotetracene, and a peri-bridged naphthalene dichalcogenide.

20 112. The electrochemical cell of claim 111, wherein said redox-active molecule is a molecule selected from the group consisting of a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrin sandwich complex, and a porphyrin array.

25 113. The electrochemical cell of claim 112, wherein said organic molecule comprises a porphyrinic macrocycle substituted at a β - position or at a *meso*- position.

114. The electrochemical cell of claim 97, wherein said second electrode has electrically coupled thereto a binding partner.

115. The electrochemical cell of claim 114, wherein said binding partner is selected from the group consisting of a nucleic acid, a protein, an antibody, a lectin, a carbohydrate, a glycoprotein.

116. The electrochemical cell of claim 97, wherein said first electrode is a
5 silver electrode, said second electrode is a gold electrode.

117. The electrochemical cell of claim 116, wherein said cell is formed on a silicon substrate.